Arabian Journal of Chemistry (2016) 9, S1660–S1664

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Thermodynamic aspects of polymer–surfactant interactions: Gemini (16-5-16)-PVP-water system

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Received 28 December 2011; accepted 21 April 2012
Available online 30 April 2012

KEYWORDS

Gemini surfactant;
Polyvinylpyrrolidone;
Critical aggregation concentration;
Critical micelle concentration

Abstract The interaction between polyvinylpyrrolidone (PVP) and gemini surfactant (16-5-16) in aqueous solution has been analyzed using conductometry. From conductivity data the critical aggregation concentration (cac), critical micelle concentration (cmc), the effective degree of counter-ion binding (β) at different temperatures were obtained. The thermodynamic parameters, i.e., Gibbs energy of aggregation and micellization, standard enthalpy of aggregation, and standard entropy of aggregation of surfactant/polymer system were estimated, employing pseudophase separation model. The negative values of Gibbs energy and standard enthalpy suggest that the surfactant/polymer aggregation process is spontaneous and exothermic respectively.

1. Introduction

Systems containing surfactants and water-soluble polymers have been a subject of extensive investigations in the last 20 years (Goddard and Ananthapadmanabhan, 1993; Hansson and Lindman, 1996; Kwak, 1998; Goddard, 2002). The mixture of polymer and surfactant is often used in the production of paints, coatings, cosmetic goods, in oil processing, and other industrial fields (Holmberg et al., 2002; Zana, 2003; Gilanyi et al., 2004). Polymer–surfactant interactions are mainly assured by a balance between hydrophobic and electrostatic interactions and involve electrostatic, dipolar or quadrupolar, hydrophobic forces. The role of the above effects is modulated by temperature and ionic strength in the stabilization of polymer–surfactant systems, is not easy to quantify. That is why the combination of experimental investigation and theoretical modeling is important. In many cases, they are only used to work their functions independently. In surfactant/polymer mixed system, polymers are used to control the rheology of solutions and suspensions, and to change the interfacial properties of solids while, surfactants are used for altering the solubilization, emulsification and wettability properties by changing the properties of the interfaces involved. When polymer and surfactant systems are present together, they can

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2012.04.015

interact to provide, either undesired or beneficial properties. These interactions can occur in both aqueous and nonaqueous systems. Many techniques such as surface tension (Jones, 1967; Schwuger, 1973), conductivity (Jones, 1967; Minatti and Zanette, 1996). viscosity (Jones, 1967; Brackman, 1991), dialysis equilibrium (Fishman and Eirich, 1971; Shirahama, 1974), ion selective electrodes (Gilanyi and Wolfram, 1981), light and neutron scattering (Brown et al., 1992), fluorescence (Zana et al., 1985), NMR (Gjerde and Hoiland, 1996), and isothermal calorimetry (da Silva et al., 2004) have been used to examine the interactions between polymer and surfactant. Furthermore, the surfactant/polymer interaction has been described at different levels of approximations such as small system thermodynamics (Gilányi, 1999), thermodynamic models (Gilanyi and Wolfram, 1981; Hall, 1985), as a chemical equilibirium, phase separation or adsorption, as well as by molecular interaction models (Nagarajan, 1985) and combination of these (Nikas and Blankschtein, 1994). Surfactant/polymer study can be classified into two methods; (i) spectroscopic method, (ii) classical physical chemical method. The first spectroscopic method can provide information about local structure and quantitative information (aggregate sizes, aggregation numbers, diffusion coefficients, solubilization parameters and kinetic parameters). The spectroscopic method covers the full range of the electromagnetic spectrum applied to the study of polymer surfactant systems. The second classical physical and chemical methods include, surface tension, binding isotherms, viscosity and rheology, phase equilibrium, dye solubilization, calorimetry, chromatographic, micellar relaxation kinetics and other separation techniques.

Now-a-days a new class of surfactant has been synthesized known as gemini or dimeric surfactant. The gemini surfactants are special type of surfactants containing two head groups and two aliphatic chains, connected by spacer group (Fig. 1).

These gemini surfactants have much greater interfacial activity (lower critical micelle concentration (cmc), higher adsorption efficiency, and better solubilizing, wetting, foaming and lime-soap dispersing properties compared to conventional surfactants (Menger and Keiper, 2000; Zana, 2002). In the present work, we have used classical physical method to investigate the thermodynamics of aggregation between gemini surfactant and polyvinylpyrrolidone (PVP) by conductometric method in aqueous medium, over a temperature range 303–318 K. The effect of temperature gives information on the relative characterization of amphiphile solutions.

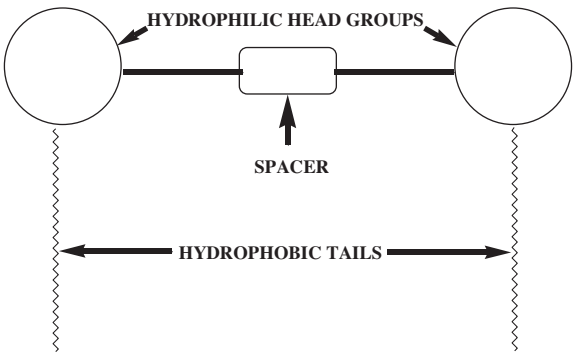


Figure 1 Structure of gemini surfactant.

This information is obtained from the thermodynamic parameters (standard Gibb's energy, enthalpy, and entropy of aggregation/micellization) that quantify the relative importance of electrostatic and hydrophobic interaction. Therefore, effect of temperature is also seen on the process of interaction between the components (gemini and polymer).

2. Experimental section

2.1. Materials and instruments

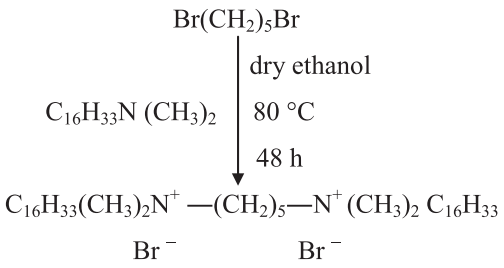
The cationic gemini surfactant with a five-methylene spacer group (16-5-16), was synthesized in our laboratory, according to usual method (De et al., 1996). For synthesis, 1,5-dibromopentane (⩾98%, Fluka, Switzerland) and N,Ndimethylhexadecylamine (⩾95%, Fluka, Switzerland) were used without further purification. The investigated polyvinylpyrrolidone, PVP K30 (M.W. ~40,000, 99.8% Fluka, Switzerland) used without further purification.

2.2. Synthesis of gemini surfactant

The molar ratio was 2.1:1 and the mixture was refluxed in ethanol for 48 h. The solvent was removed and then the raw material was recrystallized in ethanol–ethyl acetate mixtures. The crystallization was normally repeated four times. The cationic gemini of hexadecyl series with methyl spacer $-(CH_2)_5-$ was prepared according to Scheme 1. All products were checked by ^1H NMR spectroscopy using $CDCl_3$ as solvent. The overall yield was 70–80%.

2.3. Conductivity measurements

Jenway (model 4510) bridge was employed to perform the conductivity measurements. The experiments were carried out by adding progressively concentrated surfactant stock solution (pure gemini or gemini + PVP) into the thermostated solvent (dimineralized double-distilled water) at temperature ranges from 30 to 45 °C. The critical micellar concentration of the pure surfactant used was obtained from the plots of specific conductivity κ as a function of the surfactant concentration. The cmc values were taken from the intersection of the two straight lines. As in case of the 16-5-16 + PVP mixtures the plots of κ versus [surfactant] showed two breaks, the cac was determined by the intersection of first and second linear parts and the cmc in this case was the intersection point of the second and third linear parts.



Scheme 1

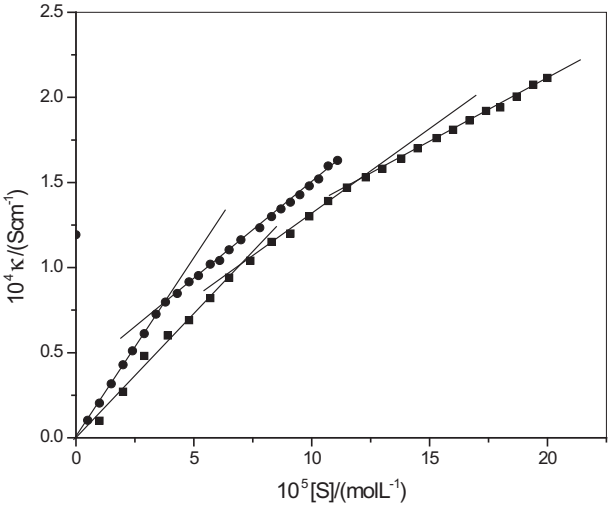


Figure 2 Plots of specific conductivity, κ of 16-5-16 in the absence of PVP (●) and in the presence (0.03 w/v%) of PVP (■) versus total surfactant concentration at 30 °C.

3. Results and discussion

3.1. Critical aggregation concentration (cac) and critical micelle concentration (cmc)

It is clear from the above figure (Fig. 2) that for gemini surfactant, the specific conductivity–concentration plots give a sharp change from the pre-micellar to the post-micellar regions at all temperatures studied. However for gemini and polyvinylpyrrolidone (PVP) systems there are two break points in conductivity–concentration profile. In case of pure surfactant, when we increase the surfactant concentration in solution then the activity of surfactant reaches a constant ''monomer solubility'' limit called cmc. If the total surfactant concentration exceeds the cmc, the monomer activity remains almost constant and the excess amount of surfactant separates into the micellar phase. When ionic surfactants interact with neutral polymers as surfactant aggregates, that is, the surfactant interaction is cooperative similar to the micelle formation. Because this cooperative nature of surfactant/polymer interaction is characterized by critical interaction concentration of the surfactant, it is called the critical aggregation concentration (cac). There is no interaction between surfactant and polymer below the cac. As the surfactant concentration exceeds the cac, the surfactant starts to bind the polymers. As the total surfactant concentration increases, the bound amount rapidly increases, which is accompanied with a slow increase of equilibrium surfactant activity. At the cmc, the polymer may be saturated with surfactant; however, the binding process is not necessarily completed at this surfactant activity. The cac is not a monomer solubility limit, because with increasing total surfactant concentration the equilibrium monomer concentration rises from the cac to the cmc. This means that with decreasing the number of available polymer binding sites, the concentration of the surfactant monomer must increase.

The cac and cmc values of pure gemini as well as with PVP are summarized in following table (Table 1).

Data represented in this table show that the cac/cmc values increase with increasing temperature. At higher temperature, the dielectric constant of solution decreases resulting in greater repulsion among the ionic head groups of surfactant molecules, which leads to increased cmc values. It is also clear from table 1 that the values of cac increase as the concentration of PVP increases, because of the amount of polymer increase, there is increase in the binding sites available to the surfactant monomer or micelle-like aggregates. Therefore, more amount of surfactant is required to bind to the polymer. After the total binding sites are occupied, the surfactant monomers become free, to form micelles.

Table 1 The values of critical aggregation concentration (cac), critical micelle concentration (cmc) and degree of micelle ionization (α_1 and α_2) for 16-5-16 + PVP at different temperature.

Temperature (K)	cac (mM)	cmc (mM)	α_1	α_2
0.0 w/v%				
303		0.0368	0.52	
308		0.0427	0.69	
313		0.0449	0.67	
318		0.0475	0.61	
0.001 w/v%				
303	0.0390	0.122	0.54	0.71
308	0.0469	0.105	0.50	0.82
313	0.0566	0.147	0.80	0.81
318	0.0646	0.150	0.75	0.92
0.01 w/v%				
303	0.0455	0.104	0.69	0.79
308	0.0540	0.118	0.51	0.88
313	0.0620	0.992	0.63	0.80
318	0.0773		0.50	
0.02 w/v%				
303	0.0559		0.45	
308	0.0653	0.149	0.50	0.80
313	0.0708	0.127	0.59	0.80
318	0.0795	0.139	0.50	0.84
0.03 w/v%				
303	0.0701	0.122	0.67	0.80
308	0.0782		0.57	
313	0.0672	0.152	0.56	0.77
318	0.0847		0.77	

3.2. Degree of counterion binding of micelles (β)

The specific binding of counterions to the micelles is a prerequisite for an understanding not only of micellization but also of all kinds of aggregation in aqueous solutions. The electrical conductivity of gemini + PVP aqueous solution is measured to study the aggregation behavior. The degree of micelle ionization was calculated by taking the ratio between slopes of the linear portion above and below the break point in the conductivity profiles. Hence two values, i.e., α_1 and α_2 were obtained in our systems (Table 1). It is clear from the table that the values of α_2 are larger; indicate increased degree of dissociation as a result of the interaction of surfactant with polymer.

3.3. Thermodynamic of micellization

The thermodynamic parameters of micellization, Gibbs energy of aggregation and Gibbs energy of micellization can be eval-

uated by using the values of cac and cmc at various temperatures (Zana, 1996). The Gibbs energy of aggregation and Gibbs energy of micellization can be calculated from the pseudophase separation model for ionic surfactants according to the following equations

$$\Delta G^{\circ}_{agg} = RT(0.5 + \beta) ln X_{cac} \quad (1)$$

$$\Delta G^{\circ}_{mic} = RT(0.5 + \beta) ln X_{cmc} \quad (2)$$

where X_{cac}/X_{cmc} are the cac/cmc in molar fraction, which is equal to cac/55.4 or cmc/55.4. The β is the degree of counterion binding to the micelles and R gas constant and T temperature. The above expression, proposed by Zana (2002), accounts for the presence of two alkyl chains and two polar head groups in the surfactant. For gemini surfactants an extra packing Gibbs energy term has to be considered, which accounts for the packing constraints of the tails. These are connected by spacer and favor micellar growth since it decreases as micellar size increases.

The standard energy of micellization of gemini surfactant in the presence of PVP was calculated at temperature range 303–318 K (Table 2). Apparently the standard free energy change of micellization of gemini surfactant in the absence and presence of PVP has negative values at all temperatures, showing that the process of micellization is a spontaneous process. The energy of transfer, ΔG_{tran}, associated with binary interaction between surfactant and polymer is given by

$$\Delta G_{tran} = \Delta G_{agg} - \Delta G_{mic} \quad (3)$$

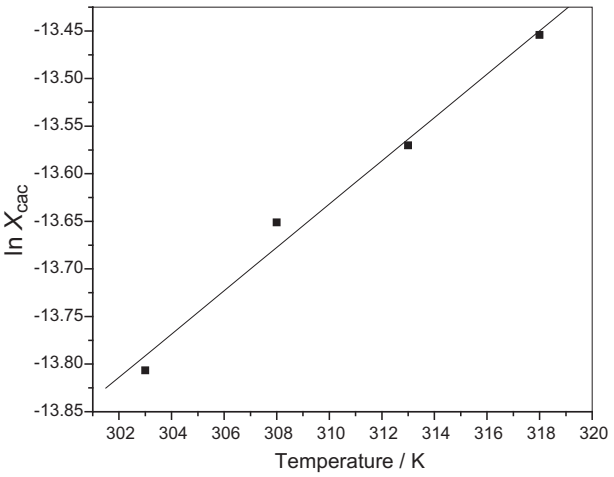


Figure 3 Variation of ln X_{cac} with temperature: at 0.02 w/v% PVP.

A negative value of ΔG_{tran} confirms the feasibility of interaction between the surfactant and polymer.

The standard enthalpy change for micelle aggregation process, ΔH_{agg}, can be determined by Gibbs–Helmholtz Eqs. (4) and (5) for aqueous solution (Fig. 3),

$$\left[\frac{\partial(\Delta^{\circ}_{agg}/T)}{\partial(1/T)}\right] = \Delta H^{\circ}_{agg} \quad (4)$$

$$\Delta H^{\circ}_{agg} = -RT^2(0.5 + \beta) ln X_{cac}/dT \quad (5)$$

Table 2 Various thermodynamic parameters for 16-5-16 + PVP at different temperature.

Temperature (K)	ΔG_{agg} (kJ mol^{-1})	ΔG_{mic} (kJ mol^{-1})	ΔG_{trans} (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
0.0 w/v%					
303		−29.025		−12.208	56
308		−29.196		−10.426	61
313		−30.294		−11.033	62
318		−32.870		−12.211	65
0.001 w/v%					
303	−34.260	−25.920	−8.339	−24.914	31
308	−35.804	−22.942	−12.862	−26.816	29
313	−25.127	−23.054	−2.072	−19.385	18
318	−27.089	−19.658	−7.432	−21.439	18
0.01 w/v%					
303	−28.592	−23.592	−4.999	−21.021	25
308	−35.088	−20.738	−14.351	−26.547	28
313	−31.023	−24.105	−6.918	−24.093	22
318	−35.645			−28.585	22
0.02 w/v%					
303	−36.520			−18.193	60
308	−34.956	−22.993	−11.963	−17.903	55
313	−32.135	−23.655	−8.480	−16.825	49
318	−35.571	−22.497	−13.074	−19.084	52
0.03 w/v%					
303	−28.395	−22.972	−5.423	−5.258	76
308	−32.080			−6.088	84
313	−33.322	−24.331	−8.991	−6.355	86
318	−25.845			−5.094	65

The standard entropy of aggregation ΔS°_{agg}, is obtained by using the following equation

$$\Delta S^{\circ}_{agg} = (\Delta H^{\circ}_{agg} - \Delta G^{\circ}_{agg})/T \quad (6)$$

The thermodynamic parameters of micellization at different temperature are listed in Table 2.

The values of standard enthalpy change for micellization are negative, inferring that the micelle formation process is exothermic. The entropy changed is positive in all cases. The positive values of ΔS°_{agg} are due to the melting of ''flickering cluster'' around the hydrocarbon tails of the surfactant and the increased randomness of hydrocarbon chains in the micellar core. The lower values of ΔS°_{agg}indicate that the restriction of free motion for micelle.

4. Conclusion

In this work, cationic gemini surfactant with five methylene spacer groups has been synthesized. The critical aggregation concentration (cac) and critical micelle concentration (cmc) were determined by electrical conductivity method. The cac or cmc at a given temperature increases with the increasing concentration of polymer. The Gibbs energy changes of aggregation/micellization of gemini surfactant in the absence and presence of PVP have negative values at all temperatures, confirmed that the process of micellization is a spontaneous process. A negative value of ΔG_{tran} confirms the feasibility of interaction between the surfactant and polymer.

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